EXPERIMENTAL STUDIES ON CONVERSION OF WASTE POLYSTYRENE TO STYRENE AND LIQUID FUEL

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
in
Chemical Engineering

By
NITIN KUMAR (10600024)

Under the Guidance of
Prof. R.K.SINGH

Department of Chemical Engineering
National Institute of Technology
Rourkela-769008, Orrisa, India
May 2010

National Institute of Technology, Rourkela

EXPERIMENTAL STUDIES ON CONVERSION OF WASTE POLYSTYRENE TO STYRENE AND LIQUID FUEL

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
in
Chemical Engineering

By
NITIN KUMAR (10600024)

Under the Guidance of
Prof. R.K.SINGH

Department of Chemical Engineering
National Institute of Technology
Rourkela-769008, Orrisa, India
May 2010

National Institute of Technology, Rourkela

CERTIFICATE

This is to certify that the thesis entitled, **"EXPERIMENTAL STUDIES ON CONVERSION OF WASTE POLYSTYRENE TO STYRENE AND LIQUID FUEL"** submitted by Mr. Nitin Kumar in partial fulfilments for the requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date

PROF. R.K.SINGH
Dept .of Chemical Engineering
National Institute of Technology
Rourkela – 769008

ACKNOWLEDGEMENT

I express my sincere gratitude to Prof. R.K.SINGH (Faculty Guide) and Prof.H.M.Jena (Project Coordinator), of Department of Chemical Engineering, National Institute of Technology, Rourkela, for their valuable guidance and timely suggestions during the entire duration of my project work, without which this work would not have been possible.

I owe a depth of gratitude to Prof. S.K. Aggarwal ,H.O.D., Department of Chemical Engineering, for all the facilities provided during the tenure of entire project work. I want to acknowledge the support of all the faculty and friends
Of Chemical Engineering Department, NIT Rourkela.

I thank to the support and good wishes of my parents and family members, without which i would not have been able to complete my thesis.

Date: 07/05/2010

Nitin Kumar

CONTENTS

Chapter 4

RESULTS AND DISCUSSIONS

ABSTRACT

The degradation of waste polystyrene sample was carried out in the temperature range of 450-575 ‘c by both thermal degradation and by catalytic degradation using SILICA-ALUMINA as catalyst. It was found that liquid product yield increases with increasing temperature in both thermal as well as catalytic degradation till 550’c , afterwards liquid product yield starts decreasing with increasing temperature. In second stage to find out optimum polystyrene : silica-alumina ratio for maximum liquid product yield , catalytic degradation of polystyrene was carried out at 550’c in various proportion, i.e. 20:1 , 15:1 , 10:1 , 5:1 and 4:1. It was found that liquid product yield increases with increasing the ratio of catalyst upto 5:1 and afterwards increasing the catalyst ratio has resulted in decreasing the amount of liquid product. It was also found that styrene was the main constituents of liquid product ,about 86 % , in thermal degradation of polystyrene at 550’c while in catalytic pyrolysis done in 5:1 ratio at the same temperature has only 41 % styrene in the liquid product obtained. This study indicates that mechanism of degradation depends on the temperature of degradation as well as amount of catalyst used for degradation.

.

List of tables

List of Figures

Chapter 1

Introduction

INTRODUCTION

Petrochemical based plastics, produced annually on the 100 million ton scale, pervade modern society as a result of their versatile and highly desirable properties. However, once disposed of, many of these plastics pose major waste management problems due to their recalcitrance.

15 million metric tons of polystyrene are produced annually worldwide, most of which ends up in landfill. Hence, the conversion of waste polystyrene (a dead end product) into a useful commodity is desirable. As a result of its widespread use and poor rate of recycling, polystyrene is viewed as a major post-consumer waste product.

In the U.S. alone, over 3 million tons of polystyrene are produced annually, 2.3 million tons of which end up in a landfill. Furthermore only 1-2% of post-consumer polystyrene waste was recycled in the U.S. in 2005. The poor rate of polystyrene recycling is due to direct competition with virgin plastic on a cost and quality basis. Consequently, there is little or no market for recycled polystyrene. As an alternative to polymer recycling, polystyrene can be burned to generate heat and energy or converted back to its monomer components for use as a liquid fuel. A number of techniques for converting plastic back to its monomer components have been developed, one of which, pyrolysis, involves thermal decomposition in the absence of air to produce pyrolysis oils or gases. In addition to their use as fuels, pyrolysis oils may also have a biotechnological use, i.e., as a starting material for the bacterial synthesis of value added products. Due to the biotechnological conversion of polystyrene to PHA, post consumer polystyrene is, potentially, a starting material for the synthesis of biodegradable plastic. Indeed this work creates a substantive link between petrochemical and biological polymers and potentially opens up a new area of exploration for the petrochemical industry.

The disposal of waste plastic materials is an extreme problem which has a high environmental impact. In the last years, there has been increasing concern about the recycling of these waste materials, for which a number of different options exist. All the alternatives have some drawbacks: for example, direct reprocessing (primary recycling) can only be applied up to a certain limit; combustion (secondary recycling) may produce harmful gases, and landfilling has environmental risks due to the chemical inertness of these materials. The tertiary recycling implies the conversion of the polymers into more valuable chemicals or fuels, technological implementations depending on the type of polymers to be recycled.

Fig 1.1 Symbol for recycled polystyrene products

Fig 1.2 common household products made from polystyrene

1.1 STYRENE

Styrene is flammable liquid ,very refractive, with a strong pungent but tolerable and quickly disappearing odour at ambient air levels of 100 ppm. The odour detection limit is around 5 ppm.

Synonyms : Vinylbenzene
Phenylethylene
Ethenylbenzene

Chemical formulae : C_8H_8 / $C_6H_5CHCH_2$

Molecular mass: 104.2

1.1.1 PHYSICAL PROPERTIES

APPEARANCE:
COLOURLESS TO YELLOW OILY LIQUID.
Boiling point: 145°C
Melting point: -30.6°C
Relative density (water = 1): 0.91
Solubility in water, g/100 ml at 20°C: 0.03
Vapour pressure, kPa at 20°C: 0.67
Relative vapour density (air = 1): 3.6
Relative density of the vapour/air-mixture at 20°C (air = 1): 1.02
Flash point: 31°C c.c.
Auto-ignition temperature: 490°C
Explosive limits, vol% in air: 0.9-6.8

Relative density: 0.9059 at 25°C
Vapour pressure: 10 mm at 35°C
Saturation vapour concentration: 6600 ppm at 20°C
Solubility: practically insoluble in water;
soluble in alcohol, ether, methanol, acetone and
carbon disulfide.
Kinematic viscosity at 20°C : 0.8 cSt
Kinematic viscosity at 100°C : 0.4 cSt
Coefficient of volume Expansion at 20°C: $0.979x10^{-3}$/°C
Specific heat at 20°C : 1.73 kJ/kg.°C

1.1.2 CHEMICAL DANGERS

The substance can form explosive peroxides. The substance may polymerize due to warming, under the influence of light, oxidants oxygen, and peroxides , causing fire and explosion hazard. Reacts

violently with strong acids, strong oxidants causing fire and explosion hazard. It Attacks rubber, copper and copper alloys.

1.1.3 OCCUPATIONAL EXPOSURE LIMITS

TLV: 20 ppm as TWA; 40 ppm as STEL; A4 (not classifiable as a human carcinogen); BEI issued (ACGIH 2005). MAK: 20 ppm, 86 mg/m³; Peak limitation category: II(2); Carcinogen category: 5; Pregnancy risk group: C.

ROUTES OF EXPOSURE:

The substance can be absorbed into the body by inhalation of its vapour.

INHALATION RISK

A harmful contamination of the air will be reached rather slowly on evaporation of this substance at 20°C.

EFFECTS OF SHORT-TERM EXPOSURE:

The substance is irritating to the eyes, the skin and the respiratory tract. Swallowing the liquid may cause aspiration into the lungs with the risk of chemical pneumonitis.The substance may cause effects on the central nervous system. Exposure at high levels may result in unconsciousness.

EFFECTS OF LONG-TERM OR REPEATED EXPOSURE:

The liquid defats the skin. The substance may have effects on the central nervous system. Exposure to the substance may enhance hearing damage caused by exposure to noise. This substance is possibly carcinogenic to humans.

Table 1.1 Hazards related to styrene

TYPES OF HAZARD / EXPOSURE	ACUTE HAZARDS / SYMPTOMS	PREVENTION	FIRST AID / FIRE FIGHTING
FIRE	Flammable. Gives off irritating or toxic fumes (or gases) in a fire.	NO open flames, NO sparks, and NO smoking.	Dry powder. Foam. Carbon dioxide.
EXPLOSION	Above 31°C explosive vapour/air mixtures may be formed. See Notes.	Above 31°C use a closed system, ventilation, and explosion-proof electrical equipment.	In case of fire: keep drums, etc., cool by spraying with water.

EXPOSURE		STRICT HYGIENE	
Inhalation	Dizziness. Drowsiness. Headache. Nausea. Vomiting. Weakness. Unconsciousness.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest. Refer for medical attention.
Skin	Redness. Pain.	Protective clothing. Protective gloves.	Remove contaminated clothes. Rinse and then wash skin with water and soap.
Eyes	Redness. Pain.	Safety goggles, or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
Ingestion	Nausea. Vomiting.	Do not eat, drink, or smoke during work.	Rinse mouth. Do NOT induce vomiting. Give plenty of water to drink. Rest.

1.1.4 ENVIRONMENTAL CONCERN

The substance is toxic to aquatic organisms. It is strongly advised that this substance should not enter the environment.

1.1.5 INDUSTRIAL APPLICATIONS

The technical material is usually 99.6% pure, and normally contains a very small amount (12 to 15 ppm) of tertiary butyl catechol as a polymerisation inhibitor. When heated to 200°C it is converted into the polymer, polystyrene. Styrene can react violently with oxidizing agents such as peroxides, strong acids, and chlorates. Fires involving styrene may release dangerous by-products specially carbon dioxiode and carbon monoxide. Fires must be extinguished with carbon dioxide or dry chemical.

Several millions of tons of styrene are used world-wide in the production of polystyrene,styrene-butadiene co-polymer for synthetic rubber,styrene-acrylonitrile polymer,acrylonitrile-butadiene-styrene copolymer,polyester resins for reinforced fiberglass products, paints,coatings, in the manufacture of reinforced plastics,and as insulators.

1.2 POLYSTYRENE

IUPAC NAME : Poly(1-phenylethane-1,2-diyl)

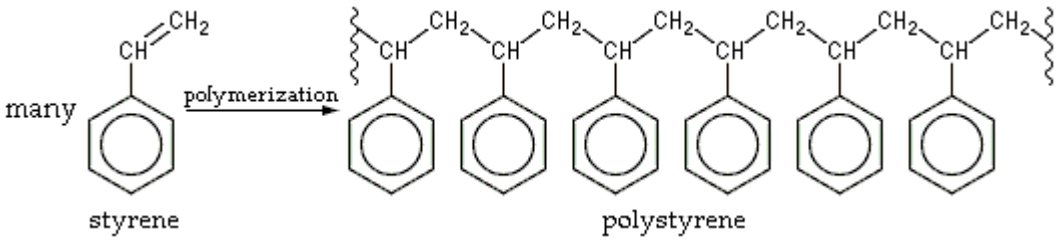
sometimes abbreviated PS, is an aromatic polymer made from the aromatic monomer styrene, a liquid hydrocarbon that is commercially manufactured from petroleum by the chemical industry. Polystyrene is one of the most widely used kinds of plastic.Polystyrene is a thermoplastic substance, which is in solid (glassy) state at room temperature, but flows if heated above its glass transition temperature (for molding or extrusion), and becoming solid again when cooling off. Pure solid polystyrene is a colorless, hard plastic with limited flexibility. It can be cast into molds with fine detail. Polystyrene can be transparent or can be made to take on various colors.

Solid polystyrene is used, for example, in disposable cutlery, plastic models, CD and DVD cases, and smoke detector housings. Products made from foamed polystyrene are nearly ubiquitous, for example packing materials, insulation, and foam drink cups.

Polystyrene can be recycled, and has the number "6" as its recycling symbol. Unrecycled polystyrene, which does not biodegrade, is often abundant in the outdoor environment, particularly along shores and waterways, and is a form of pollution.

1.2.1 GENERAL PROPERTIES

The chemical makeup of polystyrene is a long chain hydrocarbon with every other carbon connected to a phenyl group (the name given to the aromatic ring benzene, when bonded to complex carbon substituents). Polystyrene's chemical formula is (C8H8)n; it contains the chemical elements carbon and hydrogen. Because it is an aromatic hydrocarbon, it burns with an orange-yellow flame, giving off soot, as opposed to non-aromatic hydrocarbon polymers such as polyethylene, which burn with a light yellow flame (often with a blue tinge) and no soot. Complete oxidation of polystyrene produces only carbon dioxide and water vapor**.**



consider polystyrene's properties based on its structure shown above. Polystyrene is chemically unreactive (this is why it is used to create products such as containers for chemicals, solvents and foods). This stability is the result of the transformation of carbon-carbon double bonds into less reactive single bonds. The strong bonds within the molecule make styrene very stable.

Polystyrene is generally flexible and can come in the form of mouldable solids or viscous liquids. The force of attraction in polystyrene is mainly van der Waals attractions between chains. Since the molecules may have carbon chains that are thousands of atoms long the overall van der Waals attraction force is very large. Although the over all force of attraction is large, van der Waals attractions are individually very weak. It is this weakness that allows the polystyrene chains to slide along each other rendering polystyrene itself flexible and stretchable. It can be softened and moulded by heat.

1.2.2 TYPES OF POLYSTYRENE

Polystyrene is commonly produced in three forms: extruded polystyrene, expanded polystyrene foam, and extruded polystyrene foam, each with a variety of applications. Polystyrene copolymers are also produced; these contain one or more other monomers in addition to styrene. In recent years the expanded polystyrene composites with cellulose and starch have also been produced.

Properties	
Density	1050 kg/m³
Density of EPS	25-200 kg/m³
Dielectric constant	2.4–2.7
Specific gravity	1.05
Electrical conductivity (s)	10-16 S/m
Thermal conductivity (k)	0.08 W/(m·K)
Young's modulus (E)	3000-3600 MPa
Tensile strength (st)	46–60 MPa
Elongation at break	3–4%
Notch test	2–5 kJ/m²
Glass temperature	95 °C
Melting point[3]	240 °C
Vicat B	90 °C[4]
Linear expansion coefficient (a)	8 10-5 /K
Specific heat (c)	1.3 kJ/(kg·K)
Water absorption (ASTM)	0.03–0.1
Decomposition	X years, still decaying

Extruded polystyrene foam insulation is sold under the trademark Styrofoam by Dow Chemical. This term is often used informally for other foamed polystyrene products.

Polystyrene is also used in some polymer-bonded explosives.

1.2.3 Disposal and environmental issues

Polystyrene is not easily recycled because of its light weight (especially if foamed) and its low scrap value. It is generally not accepted in kerbside recycling programs. In Germany, however, polystyrene is collected, as a consequence of the packaging law (Verpackungsverordnung) that requires manufacturers to take responsibility for recycling or disposing of any packaging material they sell.

On the other hand, great advances have been made in recycling expanded polystyrene at an industrial level. Many different methods of densification have been developed.Some industrial polystyrene manufacturers accept post consumer EPS for recycling. As an example Dart Container Corporation in Mason, Michigan has an ongoing post consumer recycling operation as well as an industrial EPS scrap recycling operation.

Discarded polystyrene does not biodegrade and is resistant to photolysis.However, very little of the waste discarded in today's modern, highly engineered landfills biodegrades. Because degradation of materials creates potentially harmful liquid and gaseous by-products that could contaminate groundwater and air, today's landfills are designed to minimize contact with air and water required for degradation, thereby practically eliminating the degradation of waste.

Foamed kinds of discarded polystyrene often not only float on water, but also blow in the wind, it has the potential to be abundant in the outdoor environment due to people littering, particularly along shores and waterways**.**

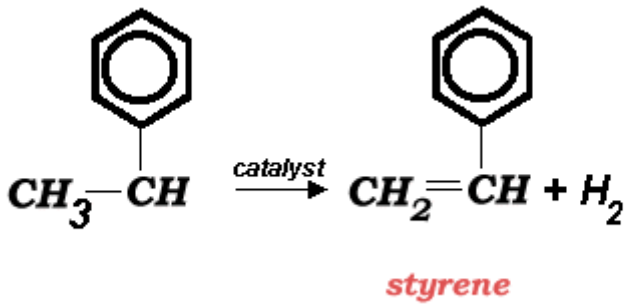
1.2.4 Incineration

If polystyrene is properly incinerated at high temperatures, the only chemicals generated are water, carbon dioxide, some volatile compounds, and carbon soot. According to the American Chemistry Council, when polystyrene is incinerated in modern facilities, the final volume is 1% of the starting volume; most of the polystyrene is converted into carbon dioxide, water vapor, and heat. Because of the amount of heat released, it is sometimes used as a power source for steam or electricity generation.

1.3 POLYMERISATION OF STYRENE

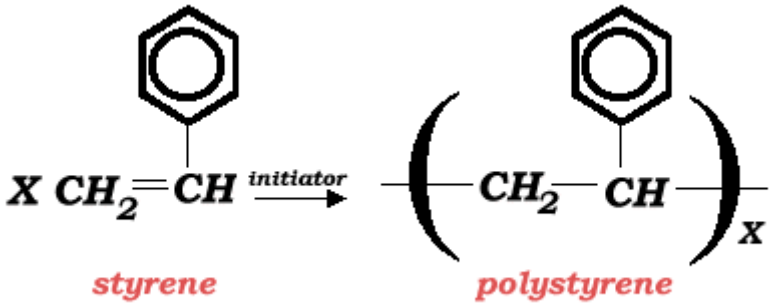
GENERAL INFORMATIONS

In 1996, world production capacity for styrene was near 19.2 million metric tonnes per year. Dow Chemical is the world's largest producer with a total capacity of 1.8 million metric tonnes in the USA, Canada, and Europe (1996 figures). The main manufacturing route to styrene is the direct catalytic dehydrogenation of ethylbenzene:



The reaction shown above has a heat of reaction of -121 KJ/mol (endothermic). Nearly 65% of all styrene is used to produce polystyrene.

The overall reaction describing the styrene polymerization is:



This reaction is carried out in an inert organic solvent environment which provides the reaction medium for this cationic polymerization reaction. The most common solvent used for this reaction is 1,2-dichloroethane (EDC). Other suitable solvents may include carbon tetrachloride, ethyl chloride, methylene dichloride, benzene, toluene, ethylbenzene, or chlorobenzene. The preferred initiator is a mixture of boron trifluoride and water.

Table 1.2 some important addition polymers and their monomers

Some Common Addition Polymers				
Name(s)	**Formula**	**Monomer**	**Properties**	**Uses**
Polyethylene low density (LDPE)	$-(CH_2\text{-}CH_2)_n-$	ethylene $CH_2=CH_2$	soft, waxy solid	film wrap, plastic bags
Polyethylene high density (HDPE)	$-(CH_2\text{-}CH_2)_n-$	ethylene $CH_2=CH_2$	rigid, translucent solid	electrical insulation bottles, toys
Polypropylene (PP) different grades	$-[CH_2\text{-}CH(CH_3)]_n-$	propylene $CH_2=CHCH_3$	atactic: soft, elastic solid isotactic: hard, strong solid	similar to LDPE carpet, upholstery
Poly(vinyl chloride) (PVC)	$-(CH_2\text{-}CHCl)_n-$	vinyl chloride $CH_2=CHCl$	strong rigid solid	pipes, siding, flooring
Poly(vinylidene chloride) (Saran A)	$-(CH_2\text{-}CCl_2)_n-$	vinylidene chloride $CH_2=CCl_2$	dense, high-melting solid	seat covers, films
Polystyrene (PS)	$-[CH_2\text{-}CH(C_6H_5)]_n-$	styrene $CH_2=CHC_6H_5$	hard, rigid, clear solid soluble in organic solvents	toys, cabinets packaging (foamed)
Polyacrylonitrile (PAN, Orlon, Acrilan)	$-(CH_2\text{-}CHCN)_n-$	acrylonitrile $CH_2=CHCN$	high-melting solid soluble in organic solvents	rugs, blankets clothing
Polytetrafluoroethylene (PTFE, Teflon)	$-(CF_2\text{-}CF_2)_n-$	tetrafluoroethylene $CF_2=CF_2$	resistant, smooth solid	non-stick surfaces electrical insulation
Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas)	$-[CH_2\text{-}C(CH_3)CO_2CH_3]_n-$	methyl methacrylate $CH_2=C(CH_3)CO_2CH_3$	hard, transparent solid	lighting covers, signs skylights
Poly(vinyl acetate) (PVAc)	$-(CH_2\text{-}CHOCOCH_3)_n-$	vinyl acetate $CH_2=CHOCOCH_3$	soft, sticky solid	latex paints, adhesives
cis-Polyisoprene natural rubber	$-[CH_2\text{-}CH=C(CH_3)\text{-}CH_2]_n-$	isoprene $CH_2=CH\text{-}C(CH_3)=CH_2$	soft, sticky solid	requires vulcanization for practical use
Polychloroprene (cis + trans) (Neoprene)	$-[CH_2\text{-}CH=CCl\text{-}CH_2]_n-$	chloroprene $CH_2=CH\text{-}CCl=CH_2$	tough, rubbery solid	synthetic rubber oil resistant

On heating or cooling most polymers undergo thermal transitions that provide insight into their morphology. These are defined as the melt transition, T_m , and the glass transition, T_g . T_m is the temperature at which crystalline domains lose their structure, or melt. As crystallinity increases, so does T_m. T_g is the temperature below which amorphous domains lose the structural mobility of the polymer chains and become rigid glasses.

T_g often depends on the history of the sample, particularly previous heat treatment, mechanical manipulation and annealing. It is sometimes interpreted as the temperature above which significant portions of polymer chains are able to slide past each other in response to an applied force. The introduction of relatively large and stiff substituents (such as benzene rings) will interfere with this chain movement, thus icreasing T_g. The introduction of small molecular compounds called plasticisers into the polymer matrix increases the interchain spacing, allowing chain movement at lower temperatures with a resulting decrease in T_g.

Table 1.3 T_m and T_g values for some common addition polymers are listed below

Polymer	LDPE	HDPE	PP	PVC	PS	PAN	PTFE	PMMA	Rubber
T_m (ºC)	110	130	175	180	175	>200	330	180	30
T_g (ºC)	-110	-110	-20	80	90	95	-110	105	-70

1.3.1 Four General Polymerization Procedures are

- Radical Polymerization : The initiator is a radical, and the propagating site of reactivity is a carbon radical.
- Cationic Polymerization : The initiator is an acid, and the propagating site of reactivity is a carbocation.
- Anionic Polymerization : The initiator is a nucleophile, and the propagating site of reactivity is a carbanion.
- Coordination Catalytic Polymerization : The initiator is a transition metal complex, and the propagating site of reactivity is a terminal catalytic complex.

Chapter 2

LITERATURE REVIEW

2.1 DEGRADATION OF POLYSTYRENE TO STYRENE

The degradation of polystyrene to styrene can be done by following methods:

I. Thermal degradation.
II. Catalytic degradation.
III. Photo-catalytic degradation.
IV. Super critical solvent oxidation method.

(1) Waste polystyrene can be converted to styrene by simple thermal degradation at 873 Kelvin but this high degradation temperature needs to be lowered by using different catalysts as it makes the conversion and recycling process expensive. The main problems of thermal degradation of polystyrene have been found to be a tendency to produce cokes and jam the apparatus, caused by the high viscosity of melting polymer and low heat transfer rate. Different methods have been used to reduce cokes.

(2) Catalytic degradation has been researched widely. By the help of suitable catalysts we can lower the temperature of thermal degradation from 873 to about 650 Kelvin in addition catalysts also make the process fast with low production of undesired products [1-9].

Table 2.1 Catalytic Degradation of polystyrene by different investigators

	Catalyst							Thermal degradation[a]
	MgO	CaO	BaO	K_2O	SiO_2/Al_2O_3	HZSM5	Active C	
BET surface area (m^2g^{-1})	47.4	1.2	0.8	–	533.9	426.0	–	–
Contents of products (wt.%)								
Oils	79.6	82.8	93.4	86.5	79.6	78.2	76.5	80.1
Cokes	8.2	4.2	0.3	3.1	6.0	5.9	10.1	–
Gases	–	–	–	–	Trace	Trace	–	–
Residues	3.8	6.5	3.2	4.1	4.2	8.5	3.8	16.1
Balance[b]	91.6	93.5	96.9	93.7	89.8	91.6	90.4	96.1
Contents of oils (wt.%)								
Styrene	79.1	75.5	76.4	77.8	59.9	64.4	70.0	70.0
Dimer	8.2	11.1	18.3	15.6	10.3	7.0	8.5	11.2
α-Methylstyrene	6.2	6.6	1.4	2.5	4.5	5.2	6.8	8.6
Toluene	3.9	3.9	1.6	2.2	2.3	3.1	4.4	5.1
Benzene	–	–	–	–	4.5	6.4	–	–
Ethylbenzene	0.7	0.9	0.2	0.3	9.0	2.0	4.3	2.4
Indan	–	–	–	–	2.2	1.8	–	–

	Catalyst					
	TiO_2	Cr_2O_3	Fe_2O_3	Co_3O_4	CuO	ZnO
BET surface area (m^2g^{-1})	150.9	–	6.7	5.9	1.6	0.7
Contents of products (wt.%)						
Oils	76.3	82.4	83.6	82.4	83.9	82.5
Cokes	9.8	5.4	4.2	3.1	2.6	2.4
Gases	–	–	–	–	–	–
Residues	5.7	4.7	4.8	6.7	4.8	6.5
Balance[a]	91.8	92.5	92.6	92.2	91.3	91.4
Contents of oils (wt.%)						
Styrene	70.0	75.5	74.3	75.9	73.5	76.1
Dimer	8.3	12.5	12.7	12.7	14.4	9.9
α-Methylstyrene	8.5	5.6	5.0	5.2	5.1	6.2
Toluene	4.1	3.3	3.6	3.3	3.1	4.0
Benzene	0.1	–	–	–	–	–
Ethylbenzene	5.5	0.8	0.7	0.6	0.7	0.7
Indan	–	–	–	–	–	–

(3) Waste polystyrene can be converted to styrene by simple photo-catalytic degradation at room temperature. The TiO2 catalyst modified by iron (II) phthalocyanine , in order to improve its photocatalytic efficiency, was used by investigators for degradation of polystyrene under the visible light irradiation as well as UV irradiation in this experiment. The main problems of photo-catalytic degradation was found to be low (30-35%) efficiency of degradation of polystyrene. It was reported by investigators that the benzene rings in PS matrix of the composite film were cleaved during UV-light irradiation [12].

(4) Supercritical water oxidation (SCWO) is a rapidly emerging-waste-treatment method that has attracted many researchers' interests. Supercritical water dissolves polystyrene, which does not dissolve in water at ambient temperature and atmospheric pressure. Various investigators obtained high yield of styrene monomer using SCWO to pyrolyse polystyrene. Though SCWO has many advantages in cracking polymeric materials, simultaneously it causes rapid corrosion to apparatus at so rigorous operating condition (temperature over 380 °C and pressure over 20 MPa).When benzene, toluene, ethylbenzene and *p*-xylene were used as supercritical solvents to depolymerise polystyrene, toluene used as supercritical solvent gave higher yields of styrene than other solvents. This implies supercritical solvents affect the reaction mechanism of polystyrene degradation differently. The conversion of polystyrene was close to complete degradation when the temperature

reached 370 °C. Supercritical degradation in toluene improved the liquid product yield close to 97% while reducing the gas and residue oil to less than 1% and 3%, respectively. Compared with thermal degradation solvent-less, supercritical toluene provides a mild environment for degradation and transfers heat from medium to the polymer chain quickly and uniformly. Benzene, toluene, ethylbenzene and *p*-xylene can be used as supercritical solvents to depolymerise polystyrene. The results of different investigators indicated solvents affected the reaction mechanism differently [10-11].

Table 2.2 Supercritical degradation of polystyrene in different solvents at 350 °C by different investigators

Supercritical solvent	Benzene	Toluene	Ethylbenzene	*p*-Xylene	Thermal
Yields of liquid (wt.%)	79.1	85.8	79.8	79.0	81.7
Compositions of liquid (wt. %)					
Benzene	–	4.21	1.79	28.4	0
Toluene	13.7	–	14.6	15.6	5.1
Ethylbenzene	24.8	3.69	–	29.2	2.4
Xylene	21.3	1.20	6.59	–	0
Styrene	33.8	88.0	49.5	18.4	70.0
α-methylstyrene	4.71	2.52	15.3	2.27	8.6
Dimer	0.36	0.38	1.20	2.02	11.2
Yields of styrene (wt. %)	26.7	75.5	39.5	14.5	57.2

Chapter 3

EXPERIMENTAL PROCEDURE

Thermal and catalytic pyrolysis of polystyrene in batch reactor

3.1 Sample preperation

1) The waste polystyrene sample materials were collected from waste yard of NIT-RKL campus.

2) The soft and high volume thermocole (expanded polystyrene) samples were first kept inside the electric oven at 80'c for one hour. This resulted in a low volume reduced hard brittle mass sample.

3) This hard brittle mass was then grounded to small pieces/powder by the help of hammer mill.

4) This powdered/small pieces of thermocole sample can now be subjected to thermal / catalytic pyrolysis.

Fig 3.1 Collected samples of waste polystyrene

Fig 3.2 Reduced polystyrene sample

Fig 3.3 Crushed polystyrene sample

3.2 Description of pyrolysis set-up

Reactor

It was a stainless steel tube of length 145 mm,internal diameter 37 mm and outer diameter 41 mm sealed at one end and an outlet tube at other end. The reactor was heated externally by putting it inside an electrical furnace.

Fig 3.4 Reactor

Furnace

The furnace used for the pyrolysis operation was an electrical furnace with the temperature being measured by a Cr:Al K type thermocouple fixed inside the furnace. The temperature of the furnace was controlled by an external PID controller.

Fig 3.5 Pyrolysis SET-UP

3.2.1 Procedure of pyrolysis：

About 15/20 grams of crushed thermocole powder were loaded in each thermal pyrolysis reaction. In the catalytic pyrolysis a mixture of catalyst and the thermocole powder in various proportions were subjected to pyrolysis in the SET-UP. The reactor was heated at the rate of 20/25 ‘c /mint up to the desired temperature. The condensable liquid product coming from the reactor was collected by passing them through the condenser and finally collecting them in the measuring flask.

The liquid product collected through the condenser was weighted and it’s volume was also noted down for each pyrolysis operation. After completion of pyrolysis operation the solid residue left out inside the reactor was weighted . Then the weight of gaseous product evolved during pyrolysis was calculated by MATERIAL BALANCE.

To know the weight loss of the sample as a function of temperature, THERMAL GRAVIMETRIC ANALYSIS TEST of the sample was done.

3.3 THERMO-GRAVIMETRIC ANALYSIS

Introduction

Thermo-gravimetric analysis or thermal gravimetric analysis (TGA) is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required.

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

3.3.1 Procedure of TG Analysis

The analyzer usually consists of a high-precision balance with a pan (generally platinum) loaded with the sample. The pan is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere may be purged with an inert gas to prevent oxidation or other undesired reactions. A computer is used to control the instrument.

Analysis is carried out by raising the temperature gradually and plotting weight (percentage) against temperature. The temperature in many testing methods routinely reaches 1000°C or greater, but the oven is so greatly insulated that an operator would not be aware of any change in temperature even if standing directly in front of the device. After the data are obtained, curve smoothing and other operations may be done such as to find the exact points of inflection [13].

3.3.2 Specific measurements made by TGA include:

- Moisture and Volatiles Content
- Composition of Multicomponent Systems
- Thermal Stability
- Oxidative Stability
- Shelf-Life Studies Using Kinetic Analysis

- Decomposition Kinetics
- Effect of Reactive Atmospheres

3.3.3 TG ANALYSIS OF WASTE POLYSTYRENE SAMPLE

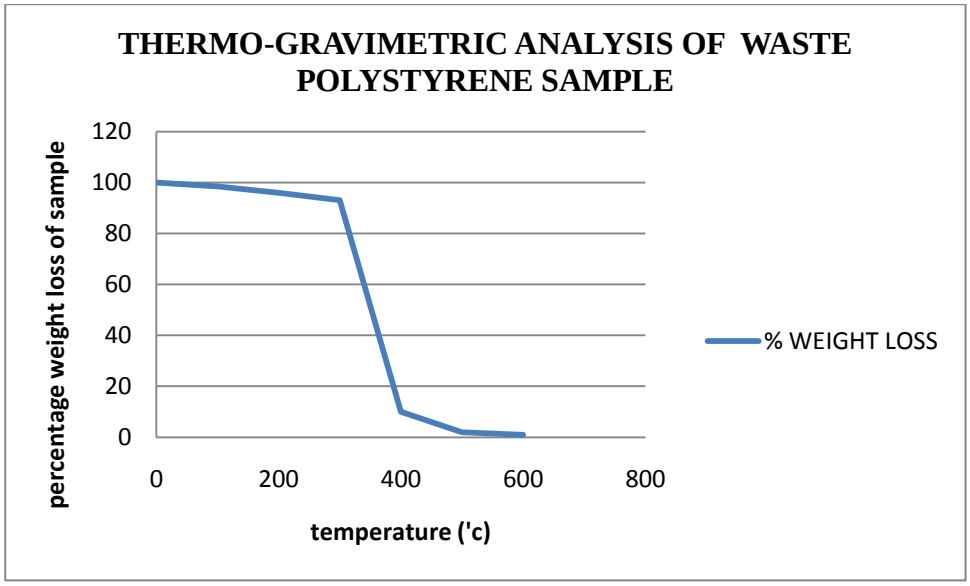


Fig 3.6 TG-Analysis of polystyrene sample

By thermo-gravimetric analysis test of waste polystyrene sample it was known that pyrolysis, both thermal and catalytic , should be done in the temperature range of 450-550 ‘c.

3.4 FOURIER TRANSFORM INFRARED SPECTROSCOPY

INTRODUCTION

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to identify different components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses.

One of the most basic tasks in spectroscopy is to characterize the spectrum of a light source: How much light is emitted at each different wavelength. The most straightforward way to measure a spectrum is to pass the light through a monochromator, an instrument that blocks all of the light except the light at a certain wavelength (the un-blocked wavelength is set by a knob on the monochromator). Then the intensity of this remaining (single-wavelength) light is measured.

The measured intensity directly indicates how much light is emitted at that wavelength. By varying the monochromator's wavelength setting, the full spectrum can be measured.

In Fourier transform spectroscopy rather than allowing only one wavelength at a time to pass through to the detector, this technique lets through a beam containing many different wavelengths of light at once, and measures the total beam intensity. Next, the beam is modified to contain a different combination of wavelengths, giving a second data point. This process is repeated many times. Afterwards, a computer takes all this data and works backwards to infer how much light there is at each wavelength.Between the light source and the detector, there is a certain configuration of mirrors that allows some wavelengths to pass through but blocks others (due to wave interference). The beam is modified for each new data point by moving one of the mirrors; this changes the set of wavelengths that can pass through.computer processing is required to turn the raw data (light intensity for each mirror position) into the desired result (light intensity for each wavelength). The processing required turns out to be a common algorithm called the Fourier transform (hence the name, "Fourier transform spectroscopy"). The raw data is sometimes called an "interferogram". The technique of "Fourier transform spectroscopy" can be used both for measuring emission spectra and absorption spectra [14].

3.4.1 Why Infrared Spectroscopy ?

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission,creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds.

To identify less common materials, IR will need to be combined with nuclear magnetic resonance, mass spectrometry, emission spectroscopy, X-ray diffraction, and/or other techniques.Infrared spectroscopy useful for several types of analysis. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present.
Informations FT-IR can provide:

• It can identify unknown materials
• It can determine the quality or consistency of a sample
• It can determine the amount of components in a mixture.

3.4.2 Physical Principles

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state (E_0) and the first excited state (E_1)]. The energy corresponding to these transitions between molecular vibrational states is generally 1-10 kilocalories/mole which corresponds to the infrared portion of the electromagnetic spectrum.

3.5 DETAILED HYDROCARBON ANALYSIS (DHA)

introduction

A gas chromatography system for the Detailed Hydrocarbon Analysis of the sample by component and by group, named DHA, is used to analyze light fractions with final boiling points up to 450°F (225°C). Samples normally analyzed using this technique are virgin napthas, alkylates, FCC gasoline, reformates (charge and product), or gases and liquids from the production of propanes and butanes. Samples containing oxygenated compounds can also be analyzed with this system.

The DHA analyzer classifies the electronic signals accumulated by the data acquisition system and uses that signal to identify individual components present in the sample. Subsequently, it reports the concentrations of the all of the groups specified by the user: Paraffins, Isoparaffins, Aromatics, Olefins, Napthens and Oxygenates. If the system is equipped with a sulfur selective detector, sulfur containing compounds present in the sample are also identified. The DHA system, is characterized by its totally interactive graphics which permit the overlay of chromatograms to discern even the smallest differences between samples.

3.5.1 GAS CHROMATOGRAPHY (GC)

Introduction

Gas chromatography (GC), is a common type of chromatography used in analytic chemistry for separating and analyzing compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance, or separating the different components of a mixture (the relative amounts of such components can also be determined). In some situations, GC may help in identifying a compound. In preparative chromatography, GC can be used to prepare pure compounds from a mixture.

3.5.2 PRINCIPLE OF GC

In a GC analysis, a known volume of gaseous or liquid analyte is injected into the "entrance" (head) of the column, usually using a microsyringe (or, solid phase microextraction fibers, or a gas source switching system). As the carrier gas sweeps the analyte molecules through the column, this motion is inhibited by the adsorption of the analyte molecules either cling onto the column walls or onto packing materials in the column. The rate at which the molecules progress along the column depends on the strength of adsorption, which in turn depends on the type of molecule and on the stationary phase materials. Since each type of molecule has a different rate of progression, the various components of the analyte mixture are separated as they progress along the column and reach the end of the column at different times (retention time). A detector is used to monitor the outlet stream from the column; thus, the time at which each component reaches the outlet and the amount of that component can be determined. Generally, substances are identified (qualitatively) by the order in which they emerge (elute) from the column and by the retention time of the analyte [15]

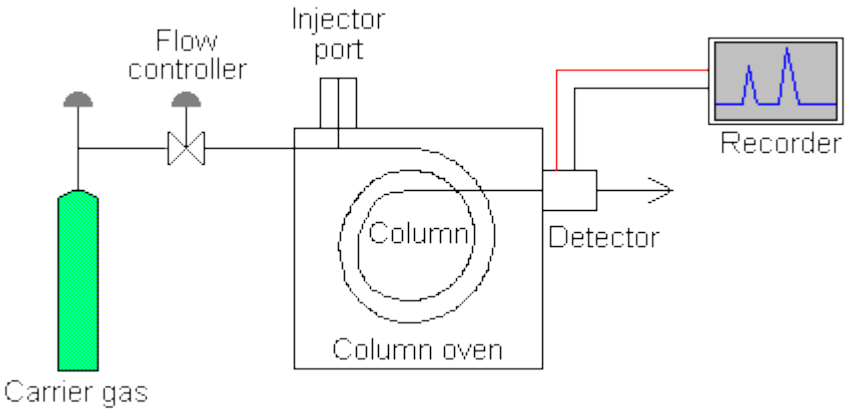


Fig 3.7 Gas chromatograph Principle

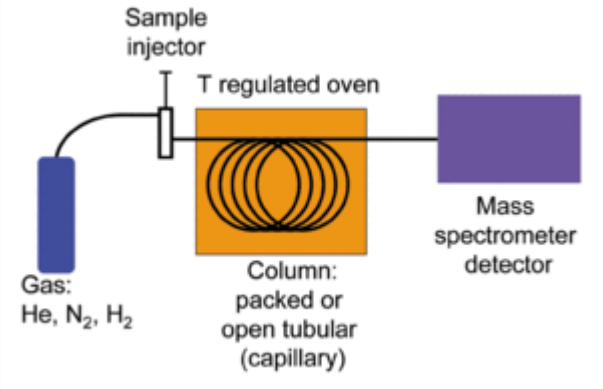


Fig 3.8 GC-MS principle

Chapter 4

RESULTS AND DISCUSSIONS

4.1 **THERMAL PYROLYSIS**

Table 4.1 OBSERVATION TABLE-1 (FOR THERMAL PYROLYSIS)

Thermal pyrolysis of 15 grams of polystyrene sample At following temp (‘c)	Weight of liquid Products obtained (grams)	Weight of solid Products obtained (grams)	Weight of gaseous Products obtained (grams)	Total time for Thermal pyrolysis (mints)
450	12.54	0.203	2.26	74
475	12.9	0.2	1.9	62
500	13.55	0.18	1.27	47
525	13.52	0.2	1.28	33
550	14.11	0.21	0.68	37
575	13.8	0.2	1.0	35

Amount of liquid product obtained in the thermal pyrolysis of 15 grams of polystyrene sample is shown below：

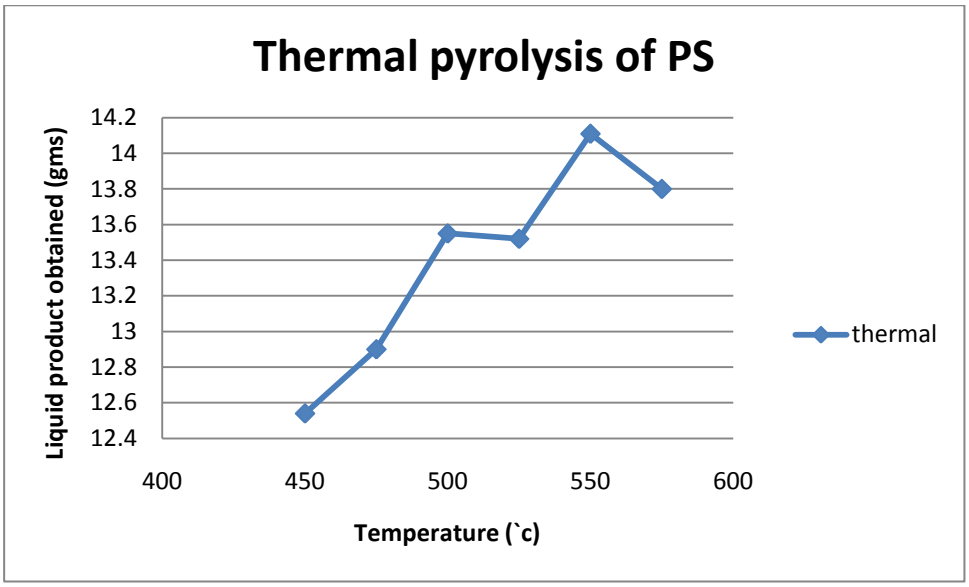


Fig 4.1 temp vs yield of liquid product in thermal pyrolysis of PS

Amount of liquid,solid and gaseous product obtained in the thermal pyrolysis of 15 grams of polystyrene sample is shown below :

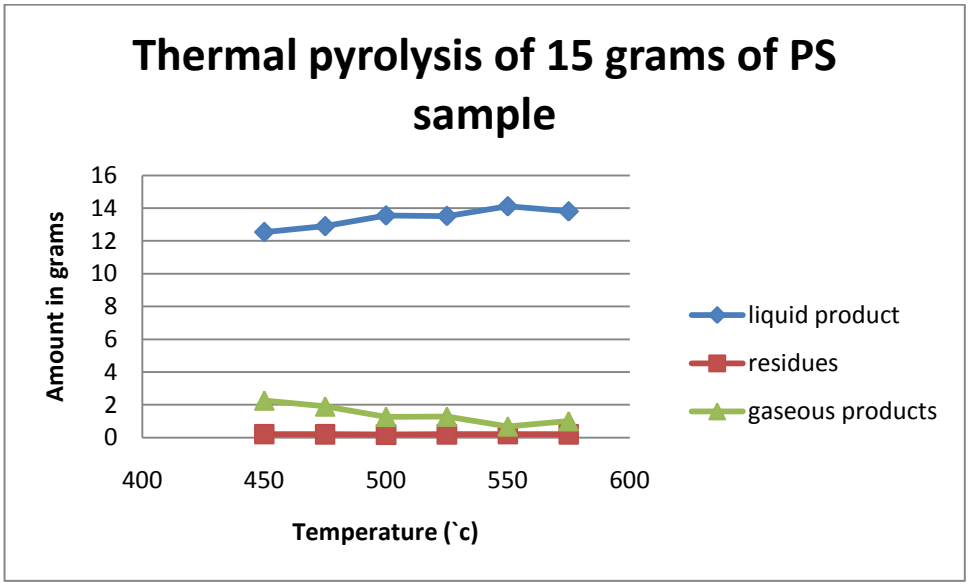


Fig 4.2 temp vs yield of liquid, solid & gaseous products in thermal pyrolysis of PS

4.2 CATALYTIC PYROLYSIS - 1

Table 4.2 OBSERVATION TABLE-2 (FOR CATALYTIC PYROLYSIS)

Catalytic pyrolysis of 15 grams of polystyrene sample With 1.5 gram silica-alumina at following temp (‘c)	Weight of liquid Products obtained (grams)	Weight of solid Products obtained (grams)	Weight of gaseous Products obtained (grams)	Total time for Thermal pyrolysis (mints)
450	12.17	1.65	2.68	68
475	12.88	1.5	2.12	60
500	13.65	0.8	2.05	38
525	13.5	1.13	1.87	38
550	13.77	1.35	1.38	35
575	13.52	1.16	1.82	31

Amount of liquid product obtained in the catalytic pyrolysis (10:1) of 15 grams of polystyrene sample is shown below

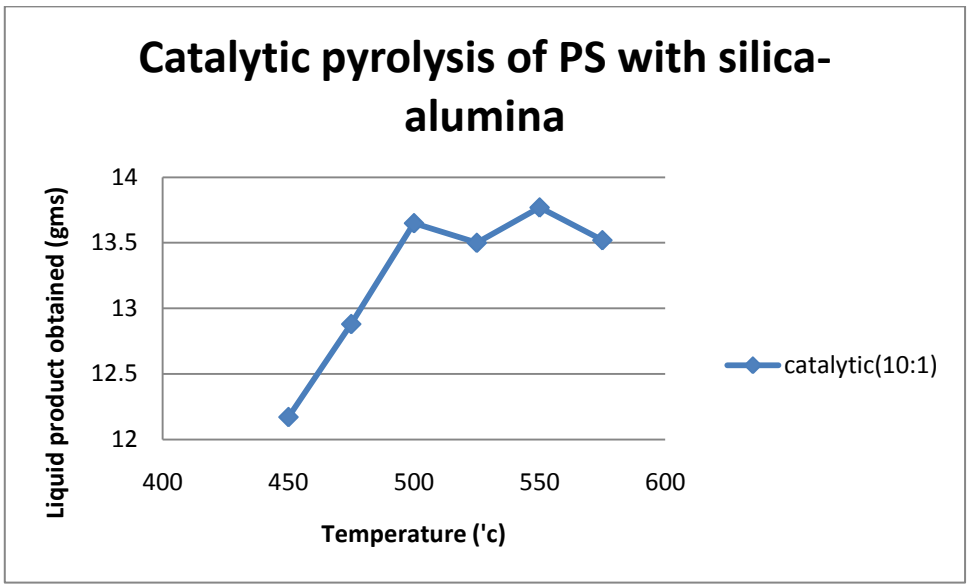


Fig 4.3 temp vs yield of liquid product in catalytic (10:1) pyrolysis of PS

Amount of liquid,solid and gaseous product obtained in the catalytic pyrolysis (10:1) of 15 grams of polystyrene sample is shown below：

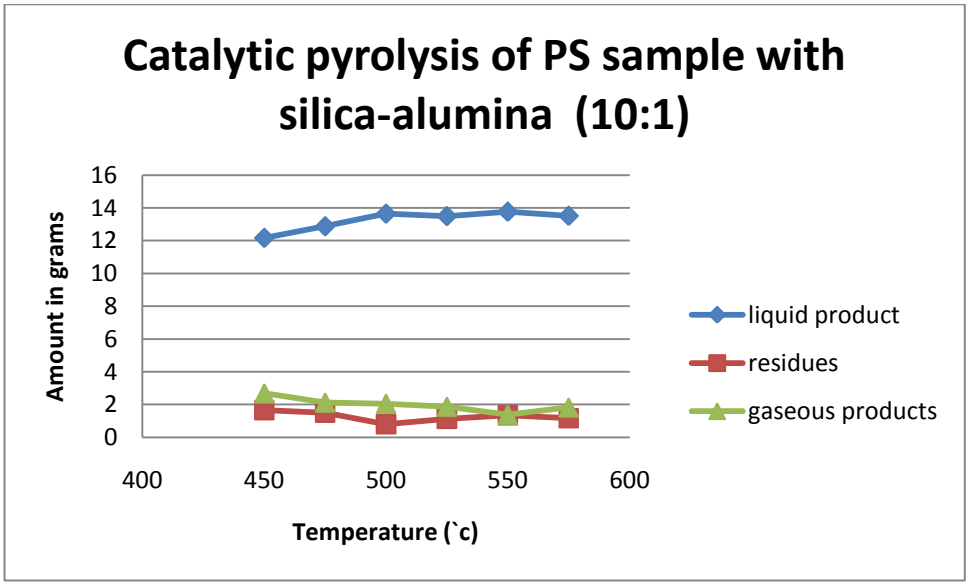


Fig 4.4 temp vs yield of liquid, solid & gaseous products in catalytic (10:1) pyrolysis of PS

Comparative study of liquid products obtained in the thermal and catalytic pyrolysis (10:1) of 15 grams of polystyrene sample is shown below：

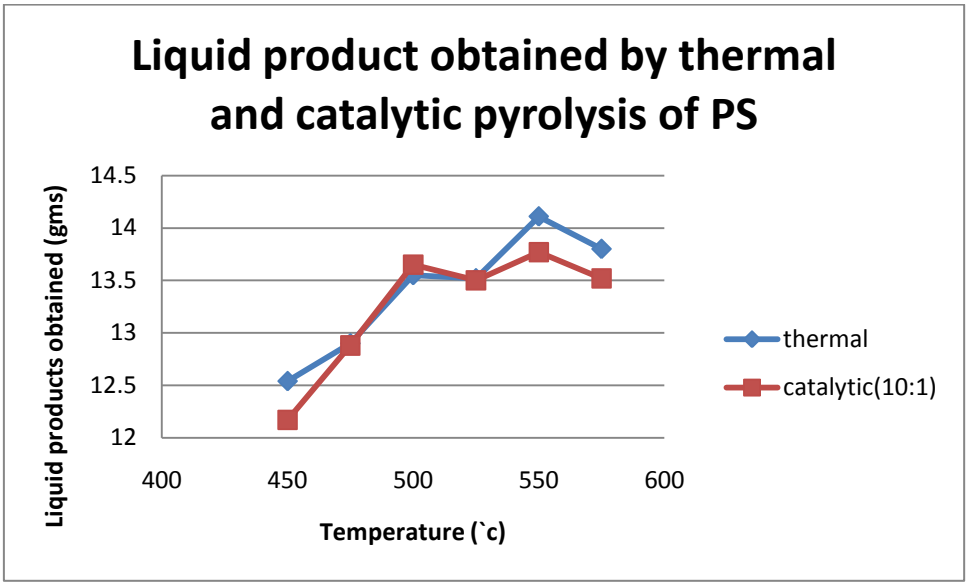


Fig 4.5 temp vs yield of liquid products in thermal as well as catalytic (10:1) pyrolysis of PS

4.3 CATALYTIC PYROLYSIS – 2

Table 4.3 OBSERVATION TABLE-3 (FOR CATALYTIC PYROLYSIS)

Catalytic pyrolysis of 15 grams of polystyrene sample at 550 ‘c with following amount of silica-alumina in grams.	Weight of liquid Products obtained (grams)	Weight of solid Products obtained (grams)	Weight of gaseous Products obtained (grams)	Total time for Thermal pyrolysis (mints)
0.75 (20 : 1)	13.42	0.95	1.38	33
1.0 (15 : 1)	13.54	1.0	1.46	33
1.50 (10 : 1)	13.77	1.35	1.38	35
3.0 (5 : 1)	14.74	2.55	0.71	31
3.75 (4 : 1)	13.30	3.4	2.05	34

Amount of liquid, solid and gaseous products obtained in the catalytic pyrolysis of 15 grams of polystyrene sample at 550 ‘c with varying amount of silica-alumina (in grams) is shown below

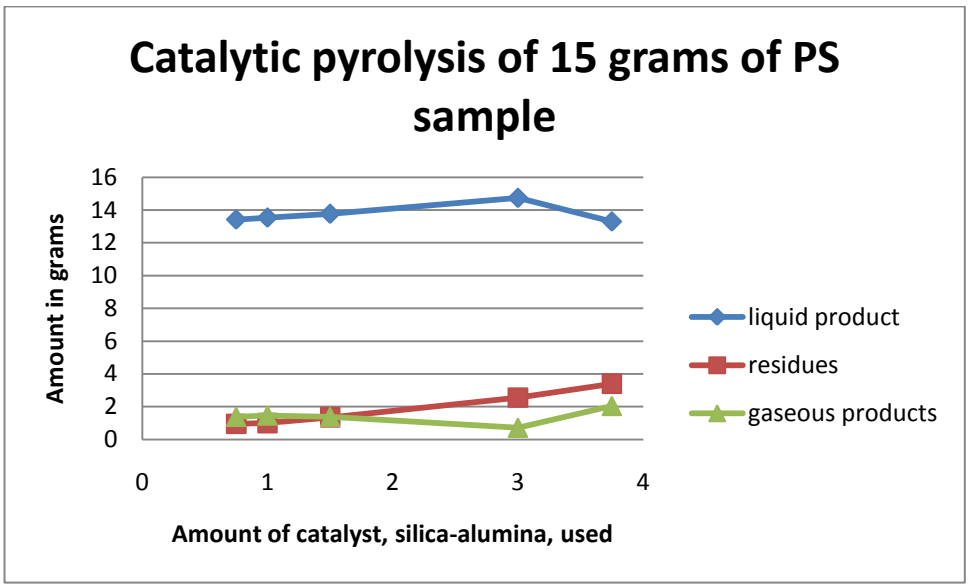


Fig 4.6 temp vs yield of liquid, solid & gaseous products in catalytic pyrolysis of PS

Amount of liquid product obtained in the catalytic pyrolysis of 15 grams of polystyrene sample at 550 ‘c with varying amount of silica-alumina (in grams) is shown below

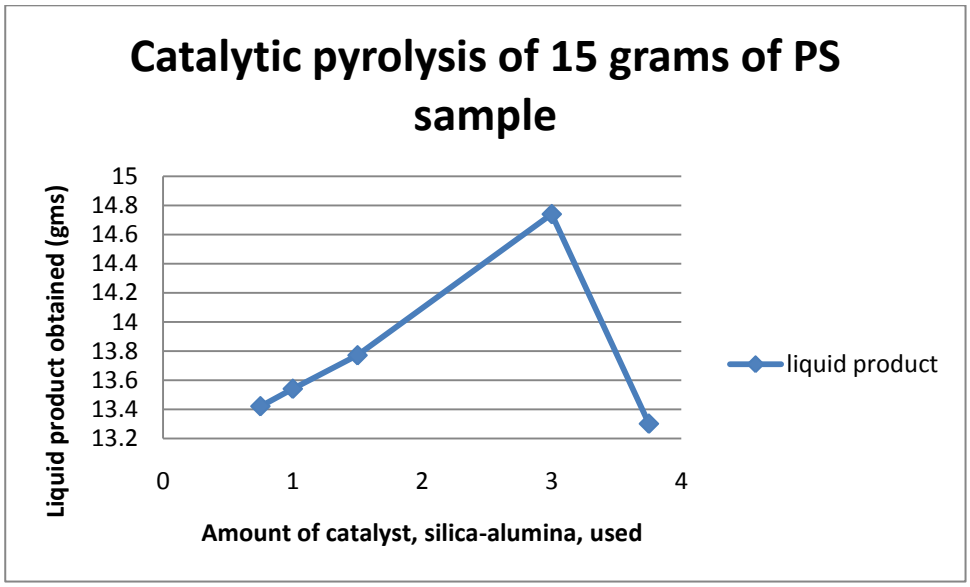


Fig 4.7 amount of SILICA-ALUMINA vs yield of liquid product in catalytic pyrolysis of PS

4.5 RESULT OF FT-IR TEST

FT-IR of the liquid product obtained by the catalytic (SILICA-ALUMINA) pyrolysis of the waste polystyrene sample at 550 ‘c. (Polystyrene : catalyst = 5 : 1)

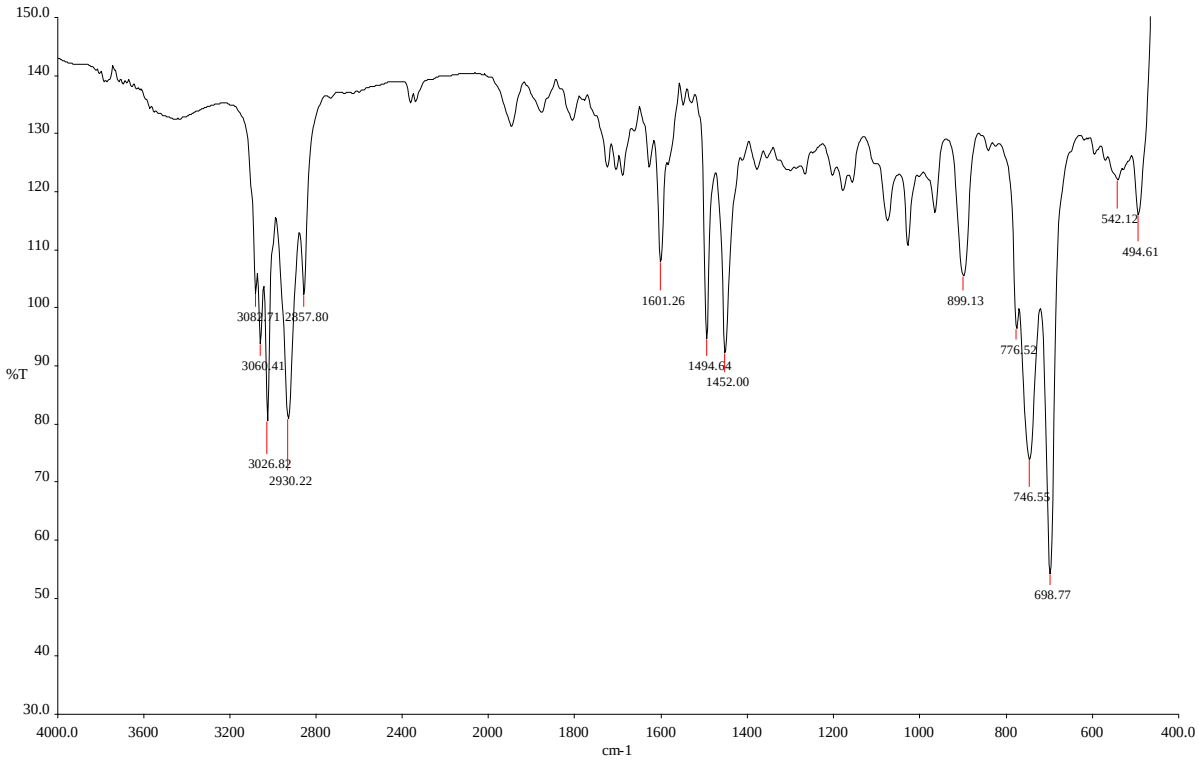


Fig 4.8 FT-IR Analysis of liquid product obtained by catalytic pyrolysis(silica-alumina) of polystyrene sample at 550`c (polystyrene : catalyst = 5 : 1)

Bands	Wave number cm^{-1}
C-Hstr Alkane	2857, 2930,
C-Hstr Aromatic ring	3026, 3060,3082
C=Cstr Alkene	1452, 1494
C-H bending Aromatic ring	899, 965
C-H bending Aromatic ring	689,746, 776

4.6 Result of DHC

The composition of liquid products obtained from thermal as well as catalytic pyrolysis (5:1) done with silica-alumina at 550'c is shown below :

Compositional analysis of Pyrolysis oil

DHA Analysis of pyrolysis oil

Composition in wt %	Thermal	Catalytic Kaoline	Catalytic Silica Alumina
C1	0	1.05	1.35
C2	0.12	2.47	1.31
C3	0.16	3.18	5.49
C4	0.06	0.49	0.46
C5	0	0	0
C6	0	0	0
Benzene	2.14	7.14	9.06
Toluene	1.9	8.1	18.21
Ethyl Benzene	6.1	12.84	20.12
Styrene	85.59	62.01	40.95
Xylene	0	0	0.4
C9- aromatics	1.12	0.2	1.3
C10+-aromatics	2.81	2.52	1.35

16 Thermolysis of waste thermocol to value added products Prof.R.K.Singh, INDIA.

Fig 4.9 DHA Analysis of liquid products obtained from thermal as well as catalytic (silica-alumina) pyrolysis (PS:catalyst=5:1) done with silica-alumina at 550'c of polystyrene sample.

4.4 PRECAUTIONS

1) Weight of sample meant for pyrolysis should be weighted carefully.

2) In case of catalytic pyrolysis sample and catalyst should be mixed thoroughly.

3) Reactor should be thoroughly cleaned of any residues,before putting the sample in it.

4) Condenser as well as measuring flask should be properly cleaned with METHANOL, to get rid of undesired chemicals present in them.

5) Reactor should be properly sealed to avoid loss of volatile component produced during pyrolysis.

6) During the process of pyrolysis keen observation should be focused on vent of reactor to know the temperature at which pyrolysis reaction started. The temperature at which reaction starts can be known by evolution of gases through vent of reactor connected to condenser.

7) When reaction starts the cold water tap connected to condenser should be turn on.

8) When pyrolysis reaction is over liquid collected in measuring flask should be properly weighted.

9) When the reactor cools down residues left should be carefully taken out and weighted properly as mass of liquid product and solid residues is used to determine the mass of gaseous products evolved during the pyrolysis reaction by the MATERIAL BALANCE equation.

Chapter 5

CONCLUSIONS

RESULTS OBTAINED FOR THERMAL AND CATALYTIC PYROLYSIS EXPERIMENTS OF POLYSYRENE

1) It was found that in case of thermal pyrolysis of polystyrene yield of liquid product increased with increasing temperature and maximum yield was obtained at 550 ‘c. After 550 ‘c yield of liquid product starts decreasing with increasing temperature.

2) It was found that in case of catalytic (10 : 1 = polystyrene : silica-alumina) pyrolysis of polystyrene yield of liquid product increased with increasing temperature and maximum yield was obtained at 550 ‘c. After 550 ‘c yield of liquid product starts decreasing with increasing temperature.

3) It was found that liquid yield was more in the case of thermal pyrolysis of polystyrene than that of catalytic pyrolysis done with SILICA-ALUMINA in 10:1 ratio.

4) It was found that with increasing catalyst ,SILICA-ALUMINA, ratio in catalytic pyrolysis of polystyrene liquid product obtained had also increased upto 5:1 ratio , i.e. when for every 5 grams of polystyrene 1 gram of catalyst was used. Afterward increasing catalyst ratio had resulted in lower yield of liquid product. Experiments done at 550’c.

5) liquid product obtained by thermal pyrolysis of PS at 550 ‘c had about 85.6 % of its constituents as monomer styrene. While liquid product obtained by catalytic pyrolysis with silica-alumina at 550’c (5 : 1 = polystyrene : silica-alumina) had about 41 % of its constituents as monomer styrene. Thus to obtain styrene from waste polystyrene thermal degradation is best method in compare to catalytic pyrolysis by silica-alumina.

RESULTS OBTAINED FOR THERMAL AND CATALYTIC PYROLYSIS EXPERIMENTS OF POLYSYRENE

6) Significant amount of benzene , toluene and ethyl benzene was obtained in catalytic pyrolysis of polystyrene done with silica-alumina at 550'c in 5:1. They constitutes 9.06 % , 18.21% and 20.12 % respectively of the total weight of the liquid products obtained. While in case of thermal pyrolysis done at 550'c they constitutes 2.14 % , 1.9 % and 6.1 % respectively of the total weight of the liquid products obtained. [RESULT FROM DHC ANALYSIS]

7) yield of lighter fractions in the liquid products was also much higher in case of catalytic pyrolysis (5:1) than in thermal pyrolysis done at 550'c. [RESULT FROM DHC ANALYSIS]

REFERENCES

[1] Congxia Xie , Fusheng Liu , Shitao Yu , Fangfei Xie , Lu Li ,Shufen Zhang , Jinzong Yang . "Study on catalytic pyrolysis of polystyrene over base modified silicon mesoporous molecular sieve". Catalysis Communications 9 (2008) 1132–1136.

[2] Vilas Ramdas Chumbhale1, Jun-Sik Kim, Sang-Bong Lee, Myoung-Jae Choi. "Catalytic degradation of expandable polystyrene waste (EPSW) over mordenite and modified mordenites". Journal of Molecular Catalysis A: Chemical 222 (2004) 133–141.

[3] Mihai Brebua, Thallada Bhaskara, Kazuya Muraia, Akinori Mutoa, Yusaku Sakataa,), Md. Azhar Uddin . " Thermal degradation of PE and PS mixed with ABS-Br and debromination of pyrolysis oil by Fe- and Ca-based catalysts". Polymer Degradation and Stability 84 (2004) 459e467.

[4] H. Ukei_, T. Hirose, S. Horikawa, Y. Takai, M. Taka, N. Azuma, A. Ueno. " Catalytic degradation of polystyrene into styrene and a design of recyclable polystyrene with dispersed catalysts". Catalysis Today 62 (2000) 67–75.

[5] N. Miskolczi, L. Bartha, Gy. Dea´k.. " Thermal degradation of polyethylene and polystyrene from the packaging industry over different catalysts into fuel-like feed stocks". Polymer Degradation and Stability 91 (2006) 517e526.

[6] Ju-Won Tae, Byung-Sik Jang, Jong-Ryeol Kim, Il Kim, Dae-Won Park. " Catalytic degradation of polystyrene using acid-treated halloysite clays". Solid State Ionics 172 (2004) 129–133.

[8] P. Carniti , A. Gervasini , P.L. Beltrame , G. Audisio , F. Bertini. "Polystyrene thermodegradation. III. Effect of acidic catalysts on radical formation and volatile product distribution". Applied Catalysis A: General 127 (1995) 139-155.

[9] Gabriela de la Puente, Ulises Sedran. " Recycling polystyrene into fuels by means of FCC: performance of various acidic catalysts". Applied Catalysis B: Environmental 19 (1998) 305-311.

[10] Huang Ke, Tang Li-hua, Zhu Zi-bin, Zhang Cheng-fang. ” Reaction mechanism of styrene monomer recovery from waste polystyrene by supercritical solvents”. Polymer Degradation and Stability 89 (2005) 312e316.

[11] Huang Ke, Tang Li-hua, Zhu Zi-bin, Zhang Cheng-fang. ” Reaction mechanism of styrene monomer recovery from waste polystyrene by supercritical solvents”. Polymer Degradation and Stability 89 (2005) 312e316.

[12] Wenjun Fa , Ling Zan , Chuqing Gong , Jiacheng Zhong , Kejian Deng. ” Solid-phase photocatalytic degradation of polystyrene with TiO2 modified by iron (II) phthalocyanine”. Applied Catalysis B: Environmental 79 (2008) 216–223.

[13] http://en.wikipedia.org/wiki/Thermogravimetric_analysis

[14]http://en.wikipedia.org/wiki/Fourier Transform Infrered Spectroscopy _analysis

[15] http://en.wikipedia.org/wiki/Detailed Hydrocarbon Analysis_analysis